AD-A119 794 AEROSPACE CORP EL SEGUNDO CA SPACE SCIENCES LAB F/G 7/4
THE AEROSPACE LONG-PATH MULTIPLE REFLECTION CELL FACILITY.(U)
AUG 82 K C HERR, L J ORTEGA, R G ROBBINS F04701-81-C-0082
UNCLASSIFIED TR-0082(2940-03)-1 SD-TR-82-60 NL

1 OF 1
AD A
119794

END
DATE
FILMED
11-82
DTIC

REPORT SD-TR-82-60

AD A119794

The Aerospace Long-Path Multiple Reflection Cell Facility

K. C. HERR, L. J. ORTEGA, R. G. ROBBINS, S. S. DURSO,
R. M. YOUNG, D. S. UREVIG, and C. J. RICE
Space Sciences Laboratory
Laboratory Operations
The Aerospace Corporation
El Segundo, Calif. 90245

30 August 1982

APPROVED FOR PUBLIC RELEASE;
DISTRIBUTION UNLIMITED

Prepared for

SPACE DIVISION
AIR FORCE SYSTEMS COMMAND
Los Angeles Air Force Station
P.O. Box 92960, Worldway Postal Center
Los Angeles, Calif. 90009

This report was submitted by The Aerospace Corporation, El Segundo, CA 90245, under Contract No. F04701-81-C-0082 with the Space Division, Deputy for Technology. P.O. Box 92960, Worldway Postal Center, Los Angeles, CA 90009. It was reviewed and approved for The Aerospace Corporation by H. R. Rugge, Director, Space Sciences Laboratory. SD/YLXT, was the project officer for Mission-Oriented Investigation and Experimentation (MOIE) Programs.

This report has been reviewed by the Public Affairs Office (PAS) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication. Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

Todd R. Frantz
Todd R. Frantz, 1st Lt, USAF
Project Officer

Florian P. Meinhardt
Florian P. Meinhardt, Lt Col, USAF
Director of Advanced Space Development

FOR THE COMMANDER

Norman W. Lee
Norman W. Lee, Jr., Colonel, USAF
Deputy for Technology

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER SD-TR-82-60	2. GOVT ACCESSION NO. AD-A119 794	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) THE AEROSPACE LONG-PATH MULTIPLE REFLECTION CELL FACILITY		5. TYPE OF REPORT & PERIOD COVERED
		6. PERFORMING ORG. REPORT NUMBER TR-0082(2940-03)-1
7. AUTHOR(s) Kenneth C. Herr, Luis J. Ortega, Richard G. Robbins, Santo S. Durso, Robert M. Young, Don S. Urevig, and Carl J. Rice		8. CONTRACT OR GRANT NUMBER(s) F04701-81-C-0082
9. PERFORMING ORGANIZATION NAME AND ADDRESS The Aerospace Corporation El Segundo, Calif. 90245		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS Space Division Air Force Systems Command Los Angeles, Calif. 90009		12. REPORT DATE 30 August 1982
		13. NUMBER OF PAGES 15
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Atmospheric Chemistry
Atmospheric Measurements
Flash Photolysis
Infrared
Infrared Spectroscopy
Long-Path Multiple Reflection Cell
White Cell

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The Aerospace long-path infrared absorption cell is described. This facility is a multiple-pass modified White cell which can be operated at any temperature between 170 K and room temperature with path lengths from 60 m up to 4 km. The cell itself is an 11-m long double-walled aluminum dewar. The spectral coverage extends from visible to 50 μm using as a source either a high temperature black-body or a tunable diode laser. An internal 20 kV flash photolysis system will permit detection and kinetic studies of transient species. This combination of characteristics makes the system ideally suited to study a wide variety of upper

DD FORM 1473 (FACSIMILE)

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

19. KEY WORDS (Continued)

20. ABSTRACT (Continued)

and lower atmospheric phenomena under realistic conditions as well as other phenomena requiring low concentrations or high sensitivity.

CONTENTS

FIGURES

INTRODUCTION

The long-path multiple reflection cell shown in Figure 1 provides the Space Sciences Laboratory with a uniquely valuable experimental facility. The cell was originally constructed for the group of Professor G. C. Pimentel in the chemistry department of the University of California, Berkeley, to aid in interpreting quantitatively the infrared spectra of the Martian atmosphere obtained by spectrometers flown on Mariner VI and Mariner VII (Herr, et al., 1970; Horn and Pimentel, 1971;). Some modifications increasing flexibility, reliability and safety have been made to the overall system since its transfer to The Aerospace Corporation.

The facility is a low-temperature multiple-pass White cell having the following capabilities:

- up to 4-km optical path length
- 170 K - 350 K operating temperature
- internal 20 kV flash photolysis system
- spectral coverage from visible to 50 μm
- blackbody and tunable diode laser sources

Experimental problems which can be addressed include studies of atmospheric transmission, atmospheric chemistry, detection of transient species, combustion reactions, vehicle exhaust plume studies and pollution reaction kinetics. All of these studies can be performed under a variety of temperature and pressure conditions.

DEWAR

The cell consists of a multiple-reflection system contained within a large double-walled aluminum vacuum chamber configured as a dewar. The dewar consists of an inner chamber (63.5-cm i.d.) serving as the sample compartment enclosed within an outer vessel (79-cm i.d.) which can be evacuated to provide thermal isolation for the inner chamber. The overall external length

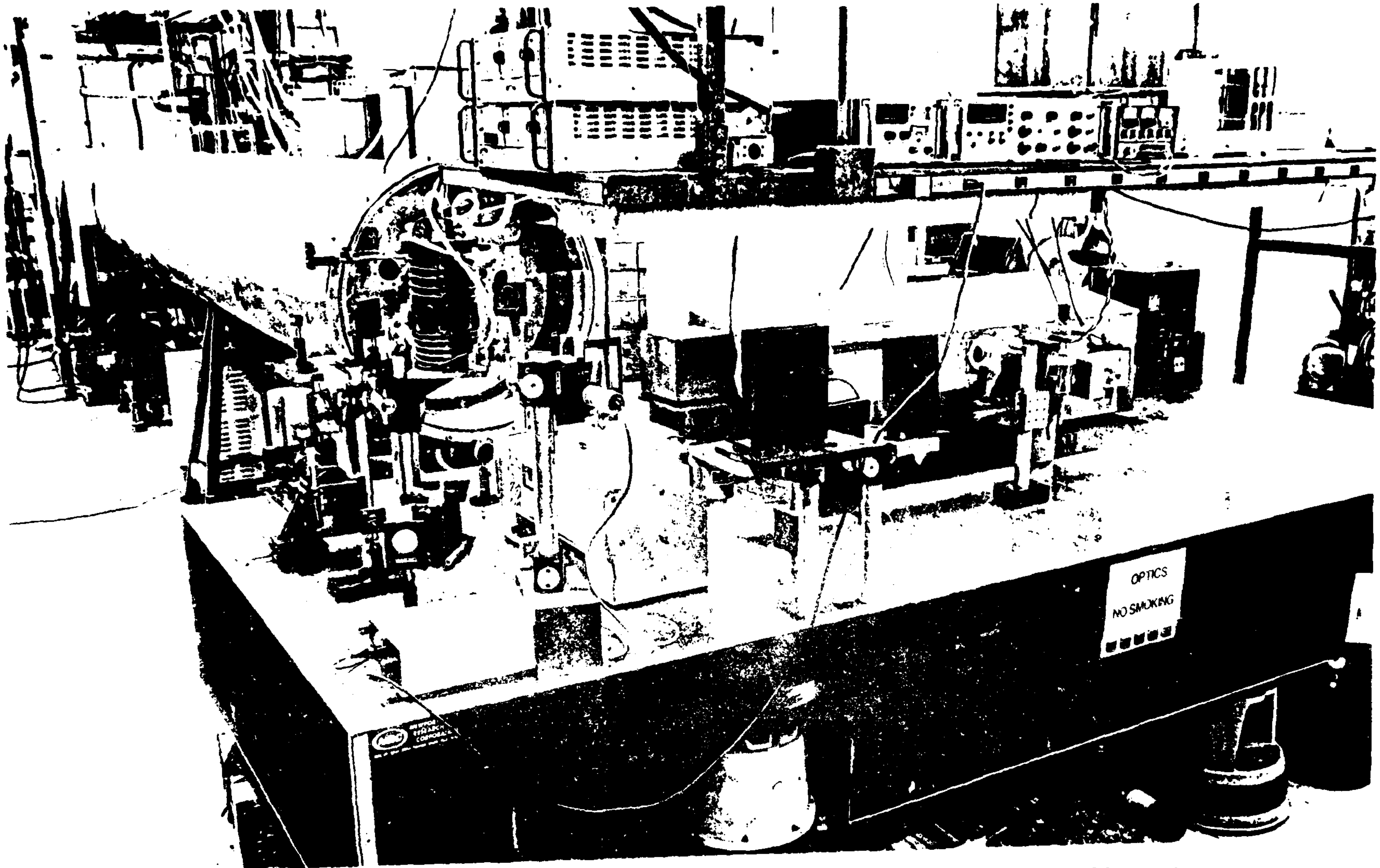

Figure. 1. Physical layout of long-path absorption cell facility. The cell itself can be seen in the background together with some of the plumbing and control wiring for the vacuum and cooling systems. The end plate of the outer vacuum chamber has been removed showing the double-wall construction. In the foreground is the optical bench which supports the external optics, tunable diode laser, blackbody source, monochromator and spectrophotometer. These same components are shown schematically in Figure 3.

is 11 m. Cooling is provided by Freon circulating in 56 cooling channels welded to the outer skin of the inner vessel. The external heat exchanger is cooled with liquid nitrogen. Cooldown from room temperature to 200 K can be accomplished in a few hours. Fine adjustments of the operating temperature are made with a 3 kW heater located in the coolant loop. This sytem provides temperature uniformity with maximum fluctuations less than 0.5°C over the entire length of the cell.

The inner vessel can be operated at pressures from ambient down to approximately 3×10^{-7} Torr; the latter pressure can be reached within a few hours. The outer vacuum is held below 10^{-5} Torr, a pressure sufficiently low to prevent any significant convective heat losses and to virtually eliminate leakage of atmospheric gases into the central chamber. Conductive heat losses are limited by a variety of special design features.

INTERNAL OPTICAL SYSTEM

The optical system is a modification of the concept originally developed by White (1942). The mirror arrangement used is shown in Figure 2. There are three concave mirrors, A, B, and C, which are configured as a conventional White cell. Normally this arrangement would produce two rows of images on mirror A. Addition of the corner mirror assembly D permits stacking four rows of images on the surface of mirror A. In Figure 2 the mirrors are shown set for 22 passes, but can in fact be set for as many as 400 permitting a total path length exceeding 4 km in the 11-m long cell. The mirrors can be adjusted externally, a provision made necessary by contraction of the optical path during cooldown.

In order to achieve a usable signal after more than 100 reflections it is absolutely essential that the reflectivity of the mirrors in the infrared

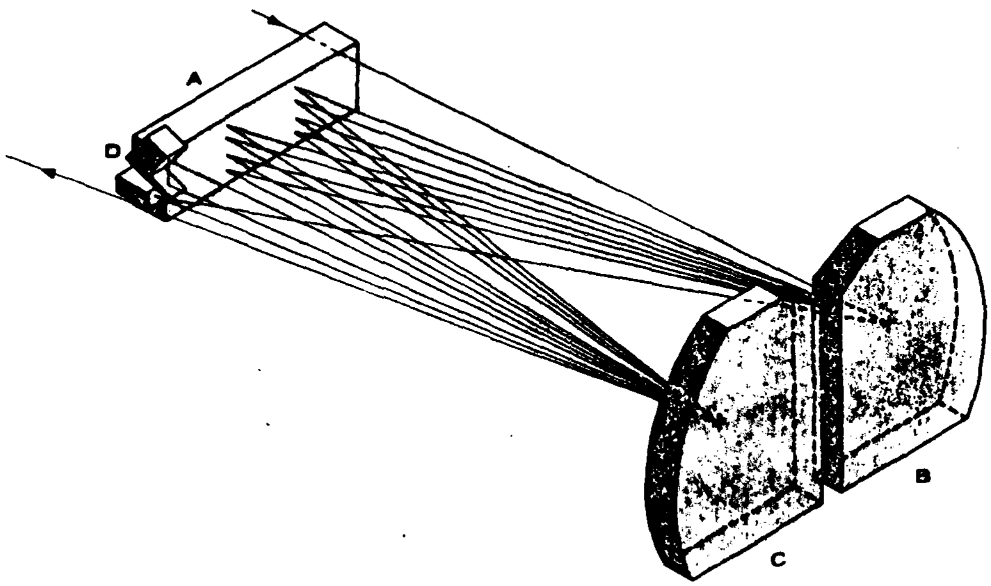

Figure 2. Internal White cell mirror configuration utilizing a corner reflector. The ray trace is for 22 passes through the cell or 220-meter total path.

be extremely high. The surface of all mirrors is evaporated gold deposited under ultra-high vacuum conditions. Reflectance values above 99% were obtained initially by this technique although there has been some degradation with time. The current value is about 98.6%.

EXTERNAL OPTICAL SYSTEM

An optical diagram of the overall facility is shown in Figure 3. Available sources include a high-intensity blackbody and a tunable diode laser, either of which can be switched into the primary optical path. Other sources can also be utilized for special purposes. The He-Ne laser is used for alignment.

Spectroscopy of stable, or slowly reacting gases, is performed with the 2050 K continuum source. After traversing the long-path cell the emerging energy is directed into a Beckman IR-7 grating spectrometer. This unit is equipped with external cooled detectors and has a scan range of 2.5 to 50 μm at 0.25 cm^{-1} resolution.

Atmospheric absorption contributed in the external optical path are effectively removed from the recorded spectrum by double beam operation. Two high-speed optically-polished metal chopper blades located at the entrance and exit windows of the cell perform this function. The detector alternately views the absorption from the cell and the external path and then that contributed just by the external path. Subtracting these signals electronically reduces the unwanted external path absorptions to less than 1% of the recorded signal level.

When extraordinary detection sensitivity is required or when transient species are to be detected (e.g., those produced by the internal 20 kilojoule flash-photolysis system) a flip-mirror is moved to permit the energy from a tunable diode laser to traverse the cell.

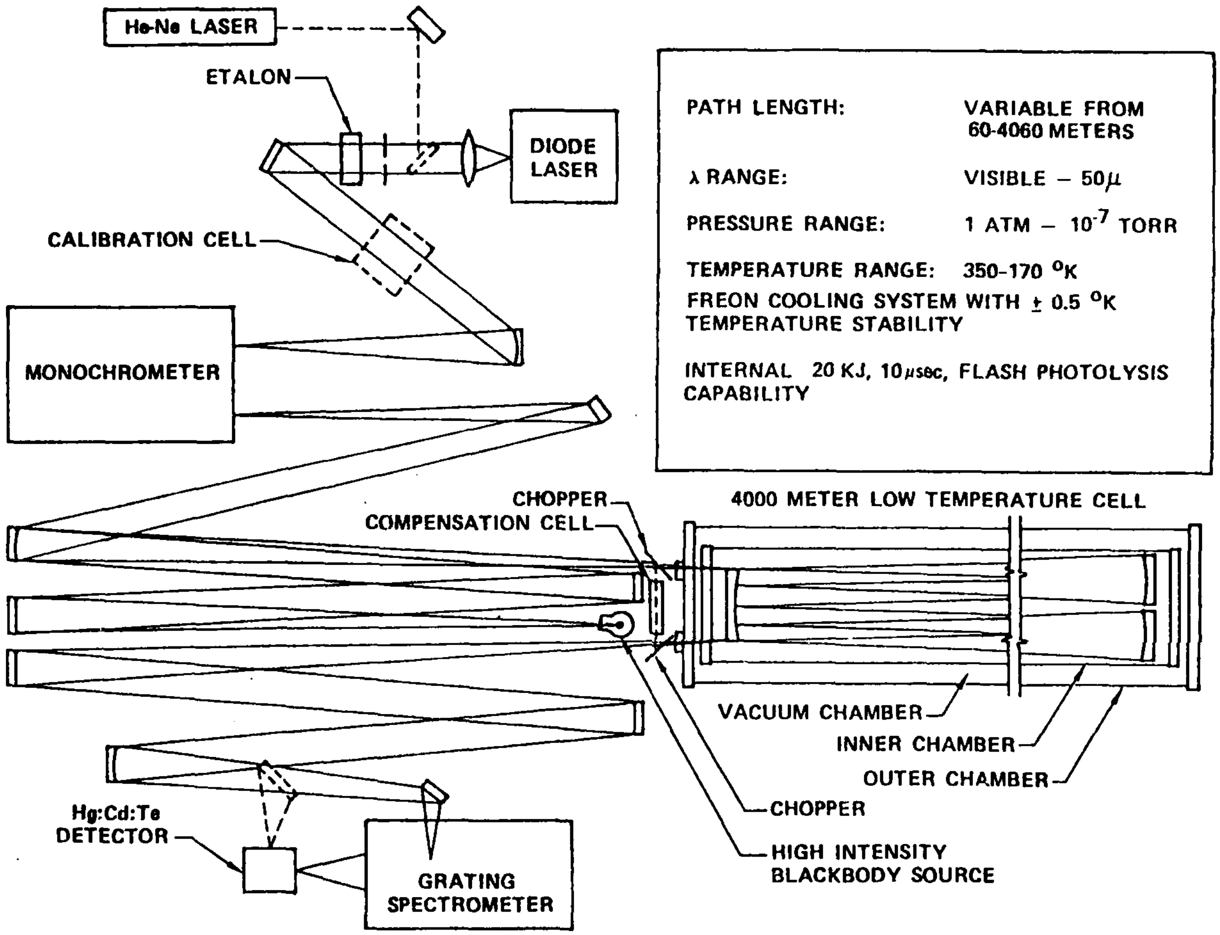

Figure 3. Optical diagram for the complete system. See the text for a description of individual components.

Tunable diode lasers can be fabricated in the wavelength range 3-30 μm. An individual diode may be tuned over a range of 50-200 cm^{-1}, although diodes with a range as great as 300 cm^{-1} have been made. Tuning is accomplished by a combination of temperature control (operating temperature: 15-100 K) for coarse tuning and current adjustment for fine tuning. The width of a single line is of the order of 3×10^{-4} cm^{-1}, though typically more than a single line is present because of multiple longitudinal modes in the diode. Whenever a single line is required, a 1/2-meter Jarrell-Ash Ebert spectrometer (labeled "monochrometer" in Figure 3) is used as a mode filter. The typical power output at any given operating wavelength is about 25 μW.

After traversing the long-path cell the emerging diode energy can be diverted directly to a cooled Hg:Cd:Te detector. When stable species are being studied and extremely small quantities of a molecular constituent are to be detected the diode laser is scanned at a slow rate. Typically 1 cm^{-1}/hour would be used. Under these conditions the double beam mode of operation would be employed to remove external path absorptions.

When transient species are being studied the diode laser scan rate is increased to 1 cm^{-1}/30 μseconds. At these rates ultra-high sensitivity is sacrificed for fast response time and the system is required to operate in the single beam mode.

INTERNAL FLASH PHOTOLYSIS SYSTEM

A major advantage of long-path absorption spectroscopy is the ability to detect extremely small quantities of gaseous molecular species. These can be stable molecules or even transient molecular intermediates if they can be produced in sufficient quantity for detection. A long-path cell provides distinct advantages for studies of molecular transients: (1) only a trace amount of the species is required and (2) the reaction rates are significantly slowed by the lower partial pressure of the reactants. For example, a free radical which exists for one μsecond in a one-meter cell will last for 4 milliseconds in a 4-km cell, assuming everything else is equal and first-order kinetics apply. This is sufficient time for more than 30 spectral scans with the tunable diode laser. Therefore, spectroscopic identification and kinetic studies of free radicals and unstable molecular reaction intermediates in the gas phase become feasible with the Aerospace long-path cell.

Production of transient species in sufficient quantities for detection will be by flash photolysis. The flash photolysis system consists of four 1.5-meter quartz flash lamps positioned along the bottom of the inner dewar, just beneath the optical envelope traversed by the multiply-reflected infrared beam. The lamps are 1.8 cm in diameter and spaced 40 centimeters apart to give uniform photon flux over nearly the full length of the cell. Reactions on the mirror surfaces are minimized by the 1.4-m separation between the outermost lamps and the optics.

The energy that is dissipated through the lamps is stored in two 8-μF Maxwell high voltage capacitors. When charged to 50 kilovolts they dissipate a total energy of 20 kilojoules in the four lamps. The optical pulse width of the discharge is expected to be less than 10 μseconds. Assuming that 1% of the available energy is converted to useful UV photons we can produce a maximum concentration throughout the cell volume of 6×10^{13} molecular intermediates/cc or approximately 1.5 microns partial pressure.

DETECTABILITY LIMITS

Detecting trace quantities of both stable and unstable gaseous molecular species is the most important capability of the Aerospace long-path infrared absorption cell. Although the ultimate sensitivity demonstrations are in progress we can project what can be expected from the results of an early experiment.

Ammonia gas was placed in the cell at 0.5 micron pressure. The ammonia lines were pressure-broadened by adding 700 mm of nitrogen. Using the continuum source, a path length of 1020 meters, and a spectral resolution of 0.6 cm^{-1}, we obtained 100% absorption with a signal-to-noise ratio (SNR) of $\sim$10/1. Since this initial measurement, improved focusing and the addition of a new Hg:Cd:Te detector has increased the SNR to 200/1. If we assume that an absorption which exceeds the noise level by a factor of three will provide positive identification of NH_3 then a partial pressure as low as .0025 micron could be detected with the continuum source. This represents a detection limit for NH_3 of $\sim$3ppb relative to atmospheric pressure using conventional spectroscopic techniques.

A significant gain in the detection capability of the system is provided by the diode laser. We should be able to realize an improvement in SNR of 700 over the continuum source at 3×10^{-4} cm^{-1} spectral resolution. In order to calculate a detectivity limit for the diode laser source we used the $_sP(1,0)$, ν_2 line of the 950 cm^{-1} NH_3 absorption band. At low pressure the line will be doppler broadened with an absorption cross-section of 96×10^{-18} cm^2. Employing a 1020-meter path length together with an integration time of one second, our detectivity should be 7×10^6 molecules/cc or 0.3ppt relative to atmospheric pressure. Tests are currently under way to measure overall system sensitivity under various conditions.

DATA ACQUISITION

Spectral data from the long-path cell are recorded in digital format. Analog-to-digital conversion is currently limited to a 12-bit format. This provides a dynamic range of 4096 to 1 which can represent either full scale spectral features or an expanded portion of the spectrum when weak absorptions are being studied. The basic computer system is a Data General NOVA 800 computer supported by a 9-track tape, a 130-megabyte disc and two linc tapes.

Survey spectra using the continuum source are digitized at a maximum rate of 1000 data points/spectrum. Slower rates are determined by clocking pulses from the spectrometer wavelength-drive system. Spectra from the tunable diode laser require a high speed digitization capability. This is provided by a 6502 microprocessor system which is capable of operating at 500 kHz; 32 K bytes of data can be rapidly stored and subsequently transferred to the NOVA computer for analysis. Extensive spectral manipulation and graphics software is currently available on the NOVA system.

LONG-PATH CELL EXPERIMENTS

After our initial demonstration of detectability limits for the system we will begin conducting a number of studies. Some of those planned or being considered are:

1) Water continuum measurements

   This will include measurements of both the self-broadening and nitrogen-broadening coefficients over as broad a temperature range as possible. A search for water dimers and trimers will be performed at low-temperature conditions.

2) Hydrogen peroxide continuum studies

   Because of its strong tendency to hydrogen bond, H_2O_2 is expected to also exhibit continuum absorption. Hydrogen peroxide is known to form a trimer and we will search for its spectrum under low-temperature conditions which favor trimer formation.

3) Hydrogen sulphide continuum

   Hydrogen sulphide does not form hydrogen bonds. A search for a continuum absorption for this molecule will be undertaken.

4) $SO_3 + H_2O \longrightarrow H_2SO_4$ kinetics

A DOE contract with the Aerospace Corporation Aerophysics Laboratory is supporting this activity. The purpose of the experiment is to obtain the gas phase rate constant. We will produce SO_3 by photolysis of O_3 in the presence of SO_2 and H_2O.

Initial experiments to determine the stability of these three gases in the long-path cell have been completed. They have shown that the mixture is stable over a period of several hours. The reaction will be initiated by the internal flash photolysis system.

5) Free radical detection

$HCCl_3 + Cl \longrightarrow CCl_3 + HCl$

Chlorine atoms produced by flash photolysis will be used to generate CCl_3 radicals by hydrogen abstraction. This experiment will utilize the ability of the long-path cell to study extremely fast kinetics of free radicals and molecular intermediates.

6) Aerosol kinetics

Photolysis of $O_3 + SO_2 + H_2O$ produces H_2SO_4. After the sulfuric acid is formed it will form an aerosol by H_2O absorption. We will be in a position to measure the kinetics of this phenomena as a function of temperature. Once the aerosol has formed image degradation measurements can be made as a function of wavelength.

SUMMARY

A coolable long-path absorption cell with up to a 4-kilometer path coupled with an internal flash-photolysis lamp is a scientifically unique system. Addition of a state-of-the-art tunable diode laser, enables the system to detect gaseous molecular species down to concentrations as low as

0.3 ppt. The remarkable sensitivity coupled with the scanning spectral capability of the diode laser makes this system an extremely valuable research tool. Chemical reactions which have been too fast to observe or elusive free radicals and molecular intermediates can now be studied. The high sensitivity of the system can also be utilized to observe extremely weak transitions of stable molecules or for trace gas detection and analysis. The capabilities of the Aerospace Long-Path Multiple Reflection Cell can be applied to many DoD programs including those which require spectroscopy of the upper and lower atmosphere, combustion studies, trace gas detection and analysis of vehicle-exhaust plumes.

REFERENCES

K. C. Herr, D. Horn, J. M. McAfee, and G. C. Pimentel, "Martian Topography from the Mariner 6 and 7 Infrared Spectra," Astron. J. 75, 883 (1970).

D. Horn and G. C. Pimentel, " 2.5-km Low-Temperature Multiple-Reflection Cell," App. Opt. 10, 1892-1898 (1971).

J. U. White, "Long Optical Paths of Large Aperture," J. Opt. Soc. Am. 32, 285 (1942).

LABORATORY OPERATIONS

The Laboratory Operations of The Aerospace Corporation is conducting experimental and theoretical investigations necessary for the evaluation and application of scientific advances to new military space systems. Versatility and flexibility have been developed to a high degree by the laboratory personnel in dealing with the many problems encountered in the nation's rapidly developing space systems. Expertise in the latest scientific developments is vital to the accomplishment of tasks related to these problems. The laboratories that contribute to this research are:

Aerophysics Laboratory: Launch vehicle and reentry aerodynamics and heat transfer, propulsion chemistry and fluid mechanics, structural mechanics, flight dynamics; high-temperature thermomechanics, gas kinetics and radiation; research in environmental chemistry and contamination; cw and pulsed chemical laser development including chemical kinetics, spectroscopy, optical resonators and beam pointing, atmospheric propagation, laser effects and countermeasures.

Chemistry and Physics Laboratory: Atmospheric chemical reactions, atmospheric optics, light scattering, state-specific chemical reactions and radiation transport in rocket plumes, applied laser spectroscopy, laser chemistry, battery electrochemistry, space vacuum and radiation effects on materials, lubrication and surface phenomena, thermionic emission, photosensitive materials and detectors, atomic frequency standards, and bioenvironmental research and monitoring.

Electronics Research Laboratory: Microelectronics, GaAs low-noise and power devices, semiconductor lasers, electromagnetic and optical propagation phenomena, quantum electronics, laser communications, lidar, and electro-optics; communication sciences, applied electronics, semiconductor crystal and device physics, radiometric imaging; millimeter-wave and microwave technology.

Information Sciences Research Office: Program verification, program translation, performance-sensitive system design, distributed architectures for spaceborne computers, fault-tolerant computer systems, artificial intelligence, and microelectronics applications.

Materials Sciences Laboratory: Development of new materials: metal matrix composites, polymers, and new forms of carbon; component failure analysis and reliability; fracture mechanics and stress corrosion; evaluation of materials in space environment; materials performance in space transportation systems; analysis of systems vulnerability and survivability in enemy-induced environments.

Space Sciences Laboratory: Atmospheric and ionospheric physics, radiation from the atmosphere, density and composition of the upper atmosphere, aurorae and airglow; magnetospheric physics, cosmic rays, generation and propagation of plasma waves in the magnetosphere; solar physics, infrared astronomy; the effects of nuclear explosions, magnetic storms, and solar activity on the earth's atmosphere, ionosphere, and magnetosphere; the effects of optical, electromagnetic, and particulate radiations in space on space systems.

DATE
FILMED

11-82